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MOST COMMON LIGANDS AND THEIR METAL COMPLEX IN NATURE

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ABSTRACT

This review will highlight recent advances in ligand design for innovative applications in medicinal inorganic chemistry. Ligands that effectively bind metal ions and also include specific features to enhance targeting, reporting, and overall efficacy are driving innovation in areas of disease diagnosis and therapy. Increasing the potency of therapeutic compounds, while limiting side-effects, is a common goal in medicinal chemistry. In an effort to achieve this goal, compounds are being developed that either target a disease site, or are activated by a disease specific biological process. Metal complexes containing targeting functions and/or bioactive ligands, as well as agents that are activated by specific enzymes, or changes in pH and pO2, provide new avenues for drug development. Radio diagnostic compounds, magnetic resonance imaging agents, and optical probes containing transition metals offer versatility unavailable to organic imaging agents. In certain cases, dual modality agents have been developed, and will be highlighted. Finally, we will discuss targeted metal binding compounds for treatment of metal overload disorders, and the recent application to neurodegenerative disease.

This article will highlight recent advances in medicinal inorganic chemistry pertaining to the use of multifunctional ligands for enhanced effect. Ligands that adequately bind metal ions and also include specific targeting features are gaining in popularity due to their ability to enhance the efficacy of less complicated metal-based agents. Moving beyond the traditional view of ligands modifying reactivity, stabilizing specific oxidation states, and contributing to substitution inertness, we will discuss recent work involving metal complexes with multifunctional ligands that target specific tissues, membrane receptors, or endogenous molecules, including enzymes.In this article we will discuss Impacts of ligands based on their metal complex in our environment. And then Utilization of ligands in pharmaceutical industries.

KEYWORDS:ligands, water, metal, Monodentate,Complex,medicine, compounds.

INTRODUCTION:

A ligand is an ion or molecule that binds to a central metal atom to form a complex (alternatively known as a coordination entity).

Ligands are usually thought of as electron donors attracted to the metal at the center of the complex. Metals are electron acceptors.**Ligand**, in chemistry, any atom or molecule attached to a central atom, usually a metallic element, in a coordination or complex compound. The atoms and molecules used as ligands are almost always those that are capable of functioning as the electron-pair donor in the electron-pair bond (a coordinate covalent bond) formed with the metal atom. Examples of common ligands are the neutral molecules water (H_2O), ammonia (NH_3), and carbon monoxide (CO) and the anions cyanide (CN^-), chloride (Cl^-), and hydroxide (OH^-). Occasionally, ligands can be cations (*e.g.,* NO^+, $N_2H_5^+$) and electron-pair acceptors. The ligands in a given complex may be identical, as the CO ligands in Fe $(CO)_5$ and the H_2O ligands in $[Ni\ (H_2O)_6]^{2+}$, or different, as the CO and NO ligands in $Co(CO)_3(NO)$. Attachment of the ligand to the metal may be through a single atom, in which case it is called a monodentate ligand, or through two or more atoms, in which case it is called a Di dentate or polydentate ligand.

Ligands may be neutral or negatively charged species with electron pairs available. Water is a common ligand. Here a water molecule is shown with its two lone pairs of electrons. An electron pair from the ligand, such as water, provides both of the electrons for the bond that forms between itself and the central metal atom or ion.

Here a single ligand L, which could be water, donates a pair of electrons to form a bond with a metal atom M.

L→M

Monodentate Ligands

Monodentate ligands have only one atom capable of binding to a central metal atom or ion.

H_20 and NH_3 are examples of neutral monodentate ligands.

When H_20 is a ligand, oxygen is the donor atom binding to the metal. When NH_3 is a ligand, nitrogen is the donor atom binding to the metal.

Examples of electrically charged monodentate ligands are halide ions, such as: F^-, Cl^-, Br^-, I^-, and cyan, CN^-.

The overall charge on a complex is the arithmetic sum of the oxidation state of the metal in the center plus the charge(s) brought to the complex by each ligand.

For example, if a complexform between Fe^{2+} and six CN^- ligands, the complex will have a -4 charge, and the formula is written $[Fe(CN)_6]^{4-}$.

Polydentate Ligands
A ligand molecule with more than one donor atom is a called a polydentate ligand. These are given specific names, depending on how many donor atoms they contain.

Bidentate Ligands

Bidentate ligands have two atoms capable of binding to a central metal atom or ion.

Ethane-1, 2-diamine is an example of a bidentate ligand.

Both of the nitrogen's in this molecule can act as electron donors, binding with a central metal atom or ionbidentate Ligands and Higher Polydentate Ligands

Tridentate ligands

Tridentate ligands have three atoms capable of binding to a central metal atom or ion.

Molecules with four donor atoms are called tetradentate ligands; five donor atoms, pentadentate; and six donor atoms hexadentate.

A complex that contains a polydentate ligand is called a chelate.

Ambidentate Ligands

Ambidentate ligands are monodentate ligands that have can bind in two possible places. For example, the nitrate ion NO_2^- can bind to the central metal atom/ion at either the nitrogen atom or one of the oxygen atoms. The thiocyanate ion, SCN^- can bind to the central metal at either the sulfur or the nitrogen.

OBJECTS OF SUPPOSSSED WORK

1) Impacts of ligands based on their metal complex in our environment.
2) Utilization of ligands in pharmaceutical industries.

REVIEW OF LITERATURE:

Slovakia [A] and Kevin J. Wilkinson
Coordination Chemistry Reviews
The chemicals and solvents were purchased from Aldrich Chemical & Co., and the solvents were purified by standard methods. Elemental analyses were carried out using a Perkin-Elmer 2400 II elemental analyzers. Molar conductance of the complexes was measured in DMSO at room temperature using a Systolic Conductivity Bridge 304. Magnetic susceptibility of the complexes was performed on a Sherwood MSB mark1 Gouy balance. Infrared spectral studies were carried out on a

Shimadzu FT IR 8000 spectrophotometer using KBr discs. UV-Vis's spectra were obtained using a THERMO SPECTRONIC 6 HEXIOS α, and fluorescence spectra were determined with an ELICO SL174 spectrofluorometer. NMR spectra were recorded on Bruker DRX-300, 300 MHz NMR spectrometer using TMS as reference. ESR spectra of the Cu(II) complex were recorded in Varian E112 machine at 300 and 77 K using tetracyanoethylene (TCNE) as the g marker. Cyclic voltametric measurement for Cu(II) complex in DMSO was carried out on an electrochemical analyzer CH Instruments (USA) using a three-electrode cell containing an Ag/AgCl reference electrode, Pt wire auxiliary electrode, and glassy carbon-working electrode with tetrabutylammonium perchlorate as supporting electrolyte. Electron-ionization (EI) mass spectra were recorded by JEOL-GC Mass Spectrometer MATE-2. The second-harmonic generation (SHG) conversion efficiency of the Schiff base ligand was determined by the modified version of powder technique in IISc, Bangalore. **XRD of copper complex was recorded using OCPL/ARD/26. SEM images were recorded in a Hitachi SEM analyzer.**

There is an obvious synergy between inorganic chemical biology and the biology of metal trafficking. Small molecule chemical tools that manipulate cellular metal content and distribution are beneficial for understanding metal trafficking pathways. At the same time, as we better understand these pathways, we can develop better strategies for intercepting them, whether it be for overcoming a metal deficiency, reducing a metal overload, or hijacking a native metal into an artificial complex with non-native function, like an enzyme inhibitor or catalytic protein inactivator. Likewise, how do cells handle unnatural metals and metal complexes? For intact metal complexes that are applied to cells or organisms, at what point does the cellular machinery differentiate the cargo from the carrier, and how does this influence where metal complexes are distributed in a cell? Finding answers to these questions will be an exciting journey into the frontier of inorganic chemistry and cell biology.

Biotic Ligand Model, a Flexible Tool for Developing Site-Specific Water Quality Guidelines for Metals

Soumya Niyogi and Chris M. Wood

Asymmetric Hydrogenation Using Monodentate Phosphonamidite Ligands

Adrian J. Minard, Ben L. Ferring, Laurent Lefort [‡]and Johannes G. de Vries

1 November 2002,

Over the past decade, several groups have targeted well-defined organometallic Group 3 metal complexes with ancillary ligand supporting environments alternative to the ubiquitous bis-Cp donor set. In addition to a desire to develop the fundamental organometallic chemistry of Group 3 bis-alkyl derivatives, these compounds are of interest as catalyst precursors for olefin and lactide polymerization processes, as well as olefin hydrazination, amination and hydrogenation cycles. This review surveys the non-Cp organometallic chemistry of the ligands which have so far been explored for this purpose, commenting on the fine balance of steric and electronic properties necessary to stabilize monomeric, base-free organometallic compounds of these metals. While *bona fide* organometallic compounds have not been explicitly prepared in all cases, promising ligands in this regard are also included. The review covers the literature from about 1994 forward, encompassing 35 new ligand systems.

Ligands Derived from Carbohydrates for Asymmetric Catalysis

Montserrat Digues Oscar Pàmies andCarmen Claver

Journal of Hazardous Materials

15 June 2012,

Biogeochemical behavior of lead (Pb), a persistent hazardous pollutant of environmental concern, strongly depends on its chemical speciation. Therefore, in this review, link between Pb speciation: presence of organic ligands and its environmental behavior has been developed. Both, biogeochemical and ecotoxicological data are discussed in environmental risk assessment context and phytoremediation studies. Three kinds of organic ligands selected for this review include: ethylene diamine tetra-acetic acid (EDTA), low molecular weight organic acids (LMWOAs) and humid substances (HSs). The review highlights the effect of Pb speciation on: (i) Pb fate and behavior in soil; (ii) Pb plant uptake and accumulation in different plant parts; and (iii) Pb-induced Phyto-toxicity. Effects of organic ligands on Pb speciation are compared: how they can change Pb speciation modifying accordingly its fate and biogeochemistry in soil-plant system? EDTA forms soluble, stable and phytoavailable Pb-chelates due to high binding Pb affinity. LMWOAs can solubilize Pb in soil by decreasing soil pH or increasing soil organic contents, but have little effect on its translocation. Due to heterogeneous structure, HSs role is complex. In consequence Pb speciation knowledge is needed to discuss Phyto-toxicity data and improved soil phytoremediation techniques.Predicting the Bioavailability of Metals and Metal Complexes: Critical Review of the Biotic Ligand Mode

MATERIAL AND METHODOLOGY:

Preparation of Ligand (CDHBHZ)

Azo Schiff base ligand (N′E)-N′-(5-((4-chlorophenyl)diazinyl)-2-hydroxybenzylidene)-2 hydroxy-benzo-hydrazide (CDHBHZ) was prepared by adding equimolar amount of 5-((4 chlorophenyl) diazinyl)-2-hydroxybenzaldehyde (1 mmol in 10 mL of ethanol) to 2-hydroxybenzohydrazide (1 mmol in 10 mL of ethanol). The mixture was refluxed while stirring for 2 hours. The formed solid product was filtered off, washed with ethanol several times followed by recrystallization from ethanol, and finally dried under vacuum.

Preparation of Metal Complexes

The metal complexes were prepared by adding equimolar amounts of salts of VO(II), Co(II), Ni(II), Cu(II), and Zn(II) (1 mmol in 20 mL of ethanol) to the azo Schiff base ligand CDHBHZ (1 mmol in 25 mL of ethanol) in the presence of 1 mmol of NaOH. The mixture was refluxed while stirring for one hour, and the resulting solid complexes were filtered off, washed several times with ethanol, followed by drying under vacuum.

Antimicrobial Study

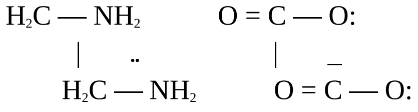
The biological activities of synthesized azo Schiff base and their metal complexes have been studied for their antibacterial and antifungal activities by well diffusion method, and the stock solution (0.001 mol) was prepared by dissolving the compounds in DMSO, and the solutions were serially diluted to find the minimum inhibitory concentration (MIC) values (μgmL^{-1}). Four bacterial stains (*Staphylococcus aureus, Escherichia coli, Pseudomonas aeruginosa, and Bacillus subtilis*) were incubated for 24 h at 37°C, and fungal stains (*Aspergillus Niger, Candida albicans, and Rhizoctonia Batticaloa*) were incubated for 48 h at 37°C. Standard antibacterial Streptomycin and antifungal drug nystatin were used for comparison under similar conditions. Antimicrobial activity studies were performed in triplicate, and the average was taken as the final reading.

NLO Study

The second-harmonic generation (SHG) conversion efficiency of the Schiff base was determined by modified version of powder technique developed by Sumathi et al. [18]. The compound was ground into powder and packed between two transparent glass slides. An Nd: YAG laser beam of wavelength 1064 nm was made to fall normally on the sample cell. The transmitted fundamental wave was absorbed by a $CuSO_4$ solution, which removes the incident 1064 nm light and Filter BG-38 also removes any residual 1064 nm light. Interference filter band width is 4 nm and for central wavelength of 532 nm. The green light is finally detected by the photomultiplier tube and displayed on the oscilloscope. The second harmonic signal was detected by a photomultiplier tube and displayed on a storage oscilloscope. The efficiency of the sample was compared with microcrystalline powder of KDP and urea. The input energy used in this particular setup is 2.2 mg./pulse.

RESULT AND DISCUSSION

The azo Schiff base ligand was prepared by reacting equimolar amounts of 5-((4-chlorophenyl) diazinyl)-2-hydroxybenzaldehyde with 2-hydroxybenzohydrazide in ethanol medium. The structures of the ligand and the complexes were established from their IR, ^{1}H-NMR spectra, elemental analyses, and magnetic susceptibility measurements. The complexes are intensely colored stable solids, and the low molar conductance values of the complexes reveal their nonelectrolyte nature. The results of the elemental analysis (Table 1) of the Schiff base are in good agreement with those calculated for the suggested formula and agree with a 1: 1 metal to ligand stoichiometry for all the complexes.



$$\begin{array}{ll} H_2C - NH_2 & O = C - O: \\ | \quad \ddot{} & | \quad \_ \\ H_2C - NH_2 & O = C - O: \end{array}$$

The structurally significant IR bands for free ligand and its complexes have been reported in Table. The free ligand exhibits IR bands at 3207 cm^{-1}ν (N–H), 1693 cm^{-1}ν (C=O), and

1620 cm^{-1} ν (C=N). The bands at 3451 and 2923 cm^{-1} in the free ligand are attributed to the free OH stretching of the diazonium moiety and phenolic moiety [19]. In the complexes, the band due to phenolic OH vibrations remained unaltered, suggesting the noninvolvement of the phenolic proton in the complex formation, whereas the band at 3451 cm^{-1} due to diazonium moiety disappeared, indicating deprotonation of the OH group and subsequent coordination of the oxygen to the metal ion. This fact was further confirmed by the ^{1}H NMR study, and this is not appropriate for all the reported complexes as most of the metal ions are paramagnetic. The band at 1620 cm^{-1} due to the azomethine group of the ligand [20] underwent a shift to lower frequency (by 1610–1589 cm^{-1}) after complexation, indicating the coordination of azomethine nitrogen to metal ion which was further confirmed by observation of the shift in the ν (N–N) stretching frequency from 1006 cm^{-1} to 1021–1047 cm^{-1} regions [20]. In all complexes, the disappearance of the band at 3207 cm^{-1}, due to ν (NH) and 1693 cm^{-1}, due to ν (C=O), supports the deprotonation of −NH proton and subsequent coordination of the oxygen of the amide carbonyl to the metal ion via enolization. This suggestion is supported by the appearance of a new band in the range 1506–1526 cm^{-1}, which may be assigned to ν (N=C–O) [21]. This finding may be due to bonding of the ligand with the metal ions through the enolic deprotonated oxygen. The appearance of the new bands in the ranges 511–526 cm^{-1} and 422–480 cm^{-1} was taken as on indication of coordination between the metal ions and the oxygen and nitrogen, respectively [5]. In addition to other bands, the vanadyl complex shows a band at 1017 cm^{-1} attributed to the V=O vibration.

TABLE OF COMMON LIGENDS

TYPE	CHARGE	LIGAND	FORMULA	NAME IN COMPLEXEX
Monodentate	Neutral	ammonia	NH3	ammine
		water	H2O	aqua
		carbon monoxide	CO	carbonyl
		pyridine	pry	pyridine
	Minus one	azide	N3-	azido
		bromide	Br-	bromide

		chloride	Cl-	chloride
		cyanide	CN-	cyanide
		fluoride	F-	fluoride
		hydroxide	OH-	hydroxide
		nitrite	NO2-	nitrite
		thiocyanate	SCN- or NCS-	thiocyanate
Bidentate	Neutral	bipyridine	Bipy	bipyridine
		ethylenediamine	En	ethylenediamine
	Minus two	carbonate	CO3-	carbonate
		oxide	O2-	oxo
		oxalate	C2O4-	oxalate
		sulfate	SO4-	sulfate

CONCLUSION:

In this work, the pharmacological effects of a few transitions metal complexes have been reviewed. The application of bioinorganic chemistry to medicine is a rapidly developing field. Novel therapeutic and diagnostic metal complexes are now having an impact on medical practice. Advances in bioinorganic chemistry are important for improving the design of compounds to reduce toxic side-effects and understand their mechanisms of action. This review reveals that the pharmacologically interesting metals such as copper, cobalt, nickel and zinc could be a suitable strategy to develop novel therapeutic tools for the medical treatment.

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